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Formaldehyde: Electronic structure calculations for the S_0 and T_1 states^{a)}

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Many-body perturbation theory (MBPT) and coupled-cluster method calculations are reported for the $S_0(X^1A_1)$ and $T_1(a^1A'')$ electronic states of formaldehyde. The structural parameters for the S_0 minimum ($R_{CH} = 1.102$ Å, $R_{CO} = 1.211$ Å, $HCH = 116.2^\circ$) and the T_1 minimum ($R_{CH} = 1.085$ Å, $R_{CO} = 1.327$ Å, $HCH = 118^\circ$, "out-of-plane" angle $= 37^\circ 12'$) agree well with experimentally deduced values. Calculated heats of reaction for dissociation to radical products and molecular products agree well with literature values. The energy barriers for dissociation to molecular products and rearrangement to hydroxycarbene are presented. Vertical and adiabatic transition energies are reported for $S_0 \rightarrow T_1$, while a vertical transition energy for $S_0 \rightarrow S_1$ is reported.

I. INTRODUCTION

Formaldehyde is an important and ubiquitous chemical species. In recent years the photochemistry resulting from excitation to the first excited singlet state S_1 has been the subject of a number of experimental¹⁻⁴ and theoretical⁵⁻⁷ reports which raise a number of important questions about interpretation of experimental data. Formaldehyde also occurs as a crucial species in models that describe the flame-zone chemistry pertinent to the combustion of carbon-containing molecules.⁸ In fact, Fifer concludes that the vapor-phase combustion of nitrate esters is dominated by the reaction sequence that describes the oxidation of formaldehyde by nitrogen dioxide.⁹

Numerous reports of theoretical studies on various electronic states of formaldehyde occur in the literature. Recent papers by Goddard and Schaefer (GS),⁵ Goddard, Yamaguchi, and Schaefer (GYS),^{7(a)} and Bell⁶ provide excellent results as well as thorough discussions of previous molecular orbital calculations.^{9,10} In particular, the results in the GS paper would support a tunneling mechanism¹¹ for the decomposition of H_2CO to $H_2 + CO$. However, the question of whether this is required to interpret the experimental results is based upon energy differences of only 4 or 5 kcal mol⁻¹. Since the CI calculations of GS⁵ and GYS^{7(a)} estimate the effects of unlinked diagrams associated with the CI quadruple excitations by the formula of Davidson,¹² and since the estimate amounts to approximately 3 kcal mol⁻¹ for formaldehyde, it seems pertinent to study the formaldehyde decomposition with many-body methods that properly treat the effects of unlinked diagrams and quadruple excitations.¹³⁻¹⁶ Consequently, dissociation energies and energy barriers are predicted by MBPT/CCD for the dissociation to radical products



molecular products



and the rearrangement to *trans*-hydroxycarbene



Other important questions pertain to the electronic excitations in formaldehyde. Equations-of-motion calculations for a number of excitation energies have been reported.^{17,18} We report here MBPT/CCD calculations for the ground (X^1A_1 , S_0) and first excited (a^1A'' , T_1) electronic states of formaldehyde. The results include equilibrium structural parameters for each state, the adiabatic excitation energy for $S_0 - T_1$, and vertical excitation energies for $S_0 - T_1$ and $S_0 - S_1$.

II. OUTLINE OF THE CALCULATIONS

For the closed-shell states included in this study, the Hartree-Fock representation of a state is given by a restricted Hartree-Fock (RHF) wave function, whereas open-shell states are described by unrestricted Hartree-Fock (UHF) wave functions. The integrals over atomic functions were computed using Dunning's 4s3p contraction of Huzinaga's 9s5p Gaussian primitive set for first-row atoms, and Dunning's scaled ($\zeta = 1.2$) 3s contraction of Huzinaga's 4s primitive set for hydrogen.^{19,20} A single set of *d*-type polarization functions augments the atomic basis sets for carbon and oxygen, with orbital exponents 0.75 and 0.85, respectively.²¹ A set of *p*-type polarization functions, with $\alpha = 1.0$, augments the hydrogen basis set.²¹ Integral calculations for the MBPT/CCD calculations were performed using the MOLCULE integral program²²; electronic structure calculations were performed using the GRNFC and UMMP programs.²³

Structural parameters for the formaldehyde conformers were obtained in several ways. Optimal parameters for the equilibrium positions on both the S_0 and T_1 surfaces were determined by fitting the results

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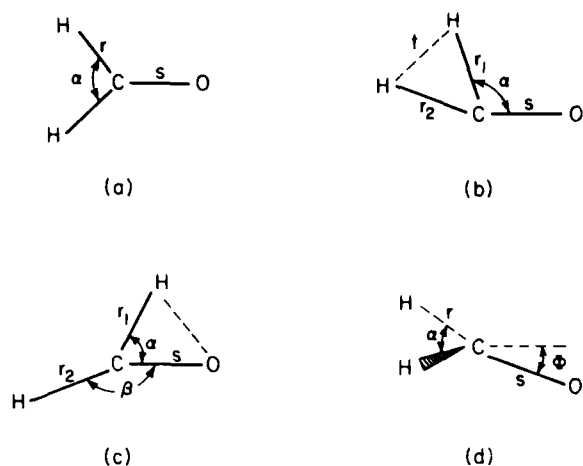


FIG. 1. Definition of structural parameters for formaldehyde calculations: (a) equilibrium, (b) molecular products transition state, (c) rearrangement transition state, (d) equilibrium for T_1 state.

of frozen-core, double-excitation MBPT (4) calculations. Such a procedure is impractical when seeking transition state structures. Structural parameters for saddlepoints on the S_0 surface resulted from analytic gradient based calculations. In particular, we used the GRADSCF computer codes.²⁴ In order to be consistent in computing energy differences on the S_0 surface, equilibrium structural parameters for formaldehyde were also determined using the GRADSCF codes. Finally, vibrational frequencies were estimated using the gradient codes. The same basis set was used for all calculations. The structural parameters for each configura-

TABLE II. Electronic structure calculations for $\text{CH}_2\text{O}(X^1A_1)$.^a

Level of theory	Structure	
	SCF	D-MBPT(4)
SCF	-113.8990	-113.8974
D-MBPT(2)	-114.2672	-114.2692
D-MBPT(3)	-114.2730	-114.2738
D-MBPT(4)	-114.2818	-114.2832
SDQ-MBPT(4)	-114.2814	-114.2830
CCD	-114.2760	-114.2772

^aUnits: hartree.

tion are depicted in Fig. 1. Theoretical and experimental structural parameters for each configuration are listed in Table I. We report dissociation energy and energy barrier results for several levels of computation: SCF; fourth-order MBPT including all double-excitation diagrams D-MBPT (4); fourth-order MBPT including all single-, double-, and quadruple-excitation diagrams SDQ-MBPT (4); and coupled cluster double calculations, CCD based upon the wave function $\exp(T_2)\Phi_0$. Excitation energies are reported at both SCF and MBPT/CCD levels of computation. All reported energies include the core electrons.

To compute dissociation energies and energy barriers requires accurate calculation of energy differences. In addition to the electronic energy, vibrational, rotational, and translational energy differences must be estimated. We assume that the rotational and translational degrees of freedom are classical. Vibrational frequencies for the various formaldehyde conformers were predicted using SCF-gradient calculations.²⁴

III. THE $S_0(X^1A_1)$ STATE OF FORMALDEHYDE

At its ground state equilibrium configuration, formaldehyde possesses C_{2v} symmetry. The structural parameters obtained by several theoretical calculations are compared with experimentally²⁵ derived values in Table I. The agreement between theory and experiment is excellent, especially for the CI calculations^{7(a)} and the MBPT results.

To determine chemical energy differences requires a high-quality *ab initio* calculation of the electronic energy of those species involved in the chemical reaction. The results of several levels of electronic structure calculation for the $S_0(X^1A_1)$ state of formaldehyde are listed in Table II. The Hartree-Fock energy for the structure determined using the gradient-based SCF calculations is lower than that corresponding to the structure found by fitting the results of D-MBPT (4) calculations. However, through fourth order, the MBPT calculations yield lower energies for the structure obtained using the D-MBPT (4) structure. In addition, the results of CCD calculations predict a lower energy for the structure determined using the D-MBPT (4) structure. Each of the SCF energies reported here is a few millihartrees lower than the single-configuration DZ + P result reported by Goddard and Schaefer.⁵ We expect, therefore, that our basis set is comparable

TABLE I. Structural parameters for formaldehyde (S_0).^a

Equilibrium configuration	r	s	α		
SCF					
This work	1.092	1.182	115.9		
DZ ^b	1.084	1.217	116.8		
DZ + P ^b	1.096	1.189	116.3		
DZ + P CI ^c	1.100	1.212	116.2		
D-MBPT(4)	1.102	1.211	116.2		
Experiment ^d	1.099	1.203	116.5		
Molecular products transition state					
	r_1	r_2	s	α	t
SCF					
This work	1.606	1.097	1.141	113.3	1.219
DZ + P ^b	1.586	1.104	1.151	112.5	1.203
DZ + P CI	1.572	1.096	1.179	110.8	1.213
Rearrangement transition state					
	r_1	r_2	s	α	β
SCF					
This work	1.213	1.095	1.266	56.4	116.6
DZ + P ^b	1.262	1.087	1.316	55.0	117.3
DZ + P CI	1.232	1.106	1.303	55.2	115.0

^aUnits: angstroms, degrees.

^bReference 5.

^cReference 7(a).

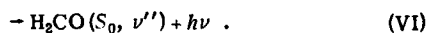
^dReference 24.

in quality to that used by GS in their initial study of the S_0 surface of formaldehyde.⁵ The two fourth-order MBPT calculations, D-MBPT (4) and SDQ-MBPT (4), agree almost exactly with one another. Clearly the contribution of the single- and quadruple-excitation diagrams almost cancel at fourth order. The fourth-order triple excitation contributions would lower the electronic energies. The CCD calculation, which includes higher order effects of double and quadruple excitations, but neglects single- and triple-excitation effects, predicts a smaller contribution of electron correlation than do the fourth-order MBPT calculations. This is due to the neglect of single- and triple-excitation effects, both of which are negative. Although CCD is not rigorously variational, since the principal terms neglected in the calculation are negative, it is quasivariational and yields the lowest energy to date for the S_0 state of formaldehyde.

IV. DISSOCIATION REACTIONS OF FORMALDEHYDE

Thermal dissociation of formaldehyde is assumed to produce radical products, hydrogen atom and formyl radical.²⁶ Interestingly, the dissociation to molecular products H_2 and CO is approximately thermoneutral, while the observed thermal dissociation energy is approximately 88 kcal mol⁻¹.²⁷ Both sets of products correlate by symmetry with the ground electronic state.

The first singlet excited state of formaldehyde [$S_1(A'1A'')$], has an excitation energy threshold lower than the threshold for thermal dissociation.¹ Photochemical studies of reactions subsequent to excitation of formaldehyde to the S_1 state are interpreted in terms of the following three processes¹:



Most investigators agree that the formation of molecular products (IV) dominates for excitation energies near the S_1 threshold (3.495 eV, 80.5 kcal mol⁻¹). The importance of the radical products channel (V) increases with increasing excitation energy.² For an excitation energy equal to 91.3 kcal mol⁻¹, the sum of quantum yields for processes (IV) and (V) is almost one, with the molecular quantum yield 0.32 ± 0.03 and the radical quantum yield 0.68 ± 0.03 .²

The crucial datum in understanding the photochemical dissociation of formaldehyde is the energy difference between the S_1 threshold (80.5 kcal mol⁻¹) and the potential energy barrier to the formation of $H_2 + CO$ on the S_0 surface. The appearance of carbon monoxide is much slower than the decay rate for S_1 , and the formation of carbon monoxide requires a collision. This behavior suggests that the high-pressure (>0.1 Torr) photochemistry of formaldehyde excited to S_1 involves a transition to an intermediate species or to a different electronic state of formaldehyde. The identity of the intermediate(s) remains a point of contention, but the results of the CI calculations by GS⁵ and GYS^{7(a)} imply that the intermediate occurs on the S_0 surface.

Goddard and Schaefer reported extensive configuration interaction calculations, including all single- and double excitations relative to their reference functions, that elucidated many features of the potential energy hypersurface that pertain to the photodissociation of formaldehyde.⁵ Subsequently, GYS^{7(a)} reinvestigated the S_0 surface using analytic gradient methods that included correlation effects. The calculations addressed reactions (IV) and (V) and the isomerization of formaldehyde to form *trans*-hydroxycarbene, all on the S_0 potential energy surface. The SD-CI study⁵ provided improved values for energy barriers to photochemical reactions of formaldehyde. A significant result of the study was the prediction that the energy required for isomerization to hydroxycarbene is only slightly greater than the energies needed for radical or molecular photodissociation.⁵ The SD-CI calculations also predicted a small energy barrier above the S_1 origin to any photochemical reaction of formaldehyde.

In subsequent research Goddard, Yamaguchi, and Schaefer^{7(a)} reported features of the formaldehyde potential energy surface using analytic configuration interaction techniques.^{26,29} The results of that research differ little from the results obtained by GS.⁵ A noteworthy conclusion of the GYS work is that the results of CI calculations using the SCF optimized geometry differs little from those obtained using the CI determined transition state. For a double zeta plus polarization basis set, the two predictions of the molecular products dissociation barrier differ by only 0.8 kcal mol⁻¹.

Miller¹¹ employed the barrier height and vibrational frequencies predicted by GS⁵ to calculate the collisionless decay rate for $S_0 \rightarrow H_2 + CO$ as a function of energy. The results of Miller's analysis suggest that S_0 can decay rapidly to molecular products even at energies as much as 10 kcal mol⁻¹ lower than the barrier height. Since that analysis, however, additional studies of the S_0 surface by Harding *et al.*,³⁰ Goddard *et al.*,^{7(a)} and this work have modified the original estimate of the vibrational frequencies for the rearrangement transition state.⁵ The effect of these studies is to reduce the barrier height for the rearrangement of formaldehyde to *trans*-hydroxycarbene relative to the barrier for molecular products dissociation.

A. $CH_2O \rightarrow CHO + H$

The theoretical investigation of the formyl radical using MBPT and CCD has been published.³¹ We report in Table III the results of those calculations that pertain to the study of the dissociation of formaldehyde. The experimental zero-point vibrational energies of formaldehyde and formyl radical are 16.2³² and 7.8

TABLE III. Electronic structure results for $HCO(X^2A')$.^a

	UHF	D-MBPT(4)	SDQ-MBPT(4)	CCD
Energy	-113.2769	-113.6343	-113.6364	-113.6288

^aUnits: hartree.

TABLE IV. Heat of reaction for the dissociation of formaldehyde to radical products.^a

Level of calculation	ΔE_{gt}	ΔE_p	ΔE_R
SCF	77.0	-8.4	68.6
D-MBPT(4)	94.8	-8.4	86.4
SDQ-MBPT(4)	93.4	-8.4	85.0
CCD	94.5	-8.4	86.1
SD-CI+QC ^b	87.4	-8.3	79.1
Experiment: Ref. 3			86.0 ± 1.0
Experiment: Ref. 27			86.7 ± 1.5

^aUnits: kcal mol⁻¹.^bReference 4. QC implies that Davidson's formula was used to estimate the effect of quadruple excitations.

kcal mol⁻¹,³³ respectively. The electronic energy of the hydrogen atom, using our basis set, is -0.49778 hartree. Goddard and Schaefer computed the zero-point energies using vibrational frequencies derived from force constants predicted by *ab initio* SCF calculations.⁵ Although the magnitude of individual frequencies differed from the experimental values, the zero-point energy difference determined from SCF theory differs little from the experimental value.

A series of computed dissociation energies is presented in Table IV. Our self-consistent field calculations predict a dissociation energy (68.6 kcal mol⁻¹) that is much lower than the experimental values^{3,34} listed in the table. The two MBPT results (D-MBPT(4), 86.4 kcal mol⁻¹; SDQ-MBPT(4), 85.0 kcal mol⁻¹) and the CCD result (86.1 kcal mol⁻¹) agree well with the experimental values,^{3,34} while the GS-CI calculations predict a dissociation energy of approximately 79 kcal mol⁻¹.⁵ The present MBPT/CCD calculations employ UHF reference functions for the radical products, while the SD-CI calculations⁵ use a two-configuration RHF-SCF root function. In the latter calculation, an estimate of higher excitation effects is obtained by using a two-configuration modification of Davidson's formula,¹² although the justification for using such a formula with a two-configuration reference is not clear.³⁵ For formaldehyde the net effect is less than 1 kcal mol⁻¹ in any event. The linked diagram and SD-CI results together demonstrate that high quality theoretical calculations can predict energy differences with good accuracy.

B. CH₂O → H₂ + CO

Since MBPT/CCD results are size-extensive, dissociation energies may be obtained without requiring

TABLE V. Summary of electronic structure results for H₂ + CO.^a

Level of calculation	Total energy
SCF	-113.8977
D-MBPT(4)	-114.2762
SDQ-MBPT(4)	-114.2780
CCD	-114.2709

^aUnits: hartree.TABLE VI. Predicted and experimental values for the dissociation of formaldehyde to molecular products.^a

Level of calculation	ΔE_{gt}	ΔE_p	ΔE_R
SCF	0.1	-7.1	-7.0
D-MBPT(4)	4.4	-7.1	-2.7
SDQ-MBPT(4)	3.1	-7.1	-4.0
CCD	3.9	-7.1	-3.2
Experiment: Ref. 36			-1.9

^aUnits: kcal mol⁻¹.

supermolecule calculations. Table V contains a summary of electronic energies for the supermolecule H₂...CO obtained by addition. The zero-point energy change, computed with experimental frequencies is -7.1 kcal mol⁻¹. Predicted heats of reaction, for T = 0 K, are gathered in Table VI. The experimental value (-1.9 kcal mol⁻¹) corresponds to the value derived from heat-of-formation data suggested by Benson,³⁶ corrected to zero degrees. The SCF results yield a heat of reaction that is more negative than that obtained from either of the MBPT or the CCD calculations. The MBPT and CCD calculations predict a heat of reaction that is less than that estimated from the thermochemical data.

In both dissociation energy estimates described here, the high-quality (DZP) *ab initio* electronic structure calculations predict dissociation energies that are below the experimentally obtained values. Since the experimental studies for these two reactions have good precision, it seems relevant to inquire whether theory will generally underestimate dissociation energies. One aspect of the computations suggests that theory will generally underestimate the change in electronic energy in going from reactant to dissociation products. The reason for this is that the finite basis sets used in the molecular calculations should be better suited to computations on the smaller product fragments than on the reactant molecule.³⁷ In a future article describing a series of hydrogen-dissociation reactions, we will report results that suggest that MBPT calculations of the quality used here predict dissociation energies that are generally low by about 1-3 kcal mol⁻¹.³⁸ In each case reported, however, the zeroth-order reference function was well-represented by a single determinant.

V. MOLECULAR PRODUCTS TRANSITION STATES

The dissociation of formaldehyde to form molecular products may occur by one of several proposed competing pathways. Two possible reaction channels were studied by Goddard and Schaefer, leading to the identification of two reaction intermediates.⁵ One of these intermediates, represented schematically in Fig. 1(b), occurs on the S₀ potential surface in the channel leading to the direct formation of molecular products. The other intermediate, represented schematically in Fig. 1(c), occurs on the S₀ potential surface in the channel leading to formation of the metastable species, hydroxycarbene. Because the dissociation energies pre-

dicted by the fourth-order MBPT and the CCD calculations differed by several kcal mol⁻¹ from the dissociation energy predicted by the SD-CI calculations,⁵ it is important to determine whether the same difference occurs for energy barrier predictions.

The calculations reported in Tables VII and VIII refer to structural parameters determined at the SCF level using the GRADSCF computer codes.³⁴ As noted by GYS,^{7(a)} the results of the barrier predictions should not be greatly affected by use of structural parameters determined from SCF results, since the transition states are well described by a single determinant wave function. The vibrational frequencies for the three formaldehyde structures, determined using our (431/31) basis set, are presented in Table IX, along with experimental values³⁹ and several other theoretical estimates.^{7(b),40} All calculations were done using basis sets that included polarization functions. Although the vibrational frequencies predicted using correlated wave function calculations agree better with experimental harmonic frequencies than do the SCF-level estimates, none of the theoretical methods succeeds in obtaining good agreement with experimental values. Yamaguchi *et al.*^{7(b)} suggest that the effects of higher excitations, perhaps unlinked cluster contributions, have a significant effect on the theoretical computation of frequencies. A study by Pople *et al.*⁴¹ supports that conclusion. Calculations for 12 vibrational frequencies using second-order Moller-Plesset theory, with a molecular basis that includes polarization functions on heavy atoms, yield results that differ, on the average, from experimental harmonic frequencies by 47.7 cm⁻¹, or 2.5%.⁴¹

It is more germane to the study of the barriers on the S₀ surface, however, to note the variation in zero-point energy differences occasioned by the different levels of theory. The results reported by GYS^{7(a)} clearly demonstrate that the zero-point energy differences shift little when different levels of theory are used. For the two barriers reported in that study, the SCF and CI calculations based upon the DZ + P basis lead to vibrational energy correction differences of 0.4 and 0.2

TABLE VII. Electronic structure calculations for the molecular products transition state.^a

Theoretical method	Electronic energy
SCF	
This work	-113.7319
DZ + P ^b	-113.7265
DZ + P CI ^b	-114.0391
D-MBPT(4) ^c	-114.1321
D-MBPT(4) ^d	-114.1310
SDQ-MBPT(4) ^d	-114.1314
CCD ^e	-114.1241
CCD ^d	-114.1230

^aUnits: hartree.

^bReference 7(a).

^cStructural parameters, Ref. 5.

^dStructural parameters, this work.

TABLE VIII. Electronic structure calculations for the rearrangement transition state.^a

Theoretical method	Electronic energy
SCF	
This work	-113.7397
DZ + P ^b	-113.7366
DZ + P CI ^b	-114.0481
D-MBPT(4) ^c	-114.1365
D-MBPT(4) ^d	-114.1365
SDQ-MBPT(4) ^d	-114.1380
CCD ^e	-114.1293
CCD ^d	-114.1295

^aUnits: hartree.

^bReference 7(a).

^cStructural parameters, Ref. 5.

^dStructural parameters, this work.

kcal mol⁻¹. Larger differences occur between the SCF and CI for the calculations that did not include polarization functions. Since our basis set is of the same quality as the DZ + P basis used by GYS^{7(a)} the zero-point energy difference predicted by our SCF calculations should be as accurate as those obtained by those authors. The zero-point energy differences were computed using the frequencies presented in Table IX. The vibrational correction for the molecular products dissociation is -5.7 kcal mol⁻¹, and that for the rearrangement reaction is -4.3 kcal mol⁻¹. These values agree well with those determined by GYS^{7(a)} and Harding *et al.*,³⁰ irrespective of the theoretical method used to estimate the frequencies.

Table X contains a summary of the predicted energy barriers for the formaldehyde reactions. We report the results of SCF, fourth-order MBPT calculations including double-excitation diagrams, and including all single-, double- and quadruple-excitation diagrams that contribute at that order, and CCD calculations. These results may be compared to the CI results,^{7(a)} the Moller-Plesset results of Harding *et al.*,³⁰ and to the predicted dissociation energy for the formation of radical products. In each case, the SCF calculations predict barriers that exceed those predicted by the correlation methods. Further, the correlated calculations agree well with one another in the prediction of the barrier heights.

Isomerization of formaldehyde to form hydroxycarbene exemplifies the 1,2-hydrogen shift, an important class of chemical reactions. A recent review by Schaefer elucidates the features of this reaction and provides a review of the experimental literature.⁴² The energy barriers predicted by the various correlated methods range from 85.7 (SDQ-MBPT) to 88.2 kcal mol⁻¹ (SD-CI).^{7(a)} Each theoretical technique predicts that the barrier to formation of molecular products exceeds the rearrangement barrier. However, the correlated predictions for this barrier range from 88.0 (RMP-4)³⁰ to 92.8 kcal mol⁻¹ (SD-CI),^{7(a)} with the difference in the barrier heights equal to approximately 3.0 kcal mol⁻¹.

TABLE IX. Vibrational frequencies: $\text{CH}_2\text{O}(S_0)$.

Equilibrium structure mode						
	$\nu_1 (a_1)$	$\nu_2 (a_1)$	$\nu_3 (a_1)$	$\nu_4 (b_1)$	$\nu_5 (b_2)$	$\nu_6 (b_2)$
Experiment ^a	2944	1764	1563	1191	3009	1287
Experiment ^b	2782	1746	1500	1167	2843	1247
SCF						
This work	3191	2004	1659	1343	3113	1368
Ref. 7(b)	3149	2006	1656	1335	3226	1367
Ref. 40	2971.2	1882.6	1600.1	1301.4	3070.6	1349.7
DZ + P CI [Ref. 7(b)]	3074	1869	1596	1243	3155	1306
CEPA	2925.6	1797.2	1580.9	1220.9	3032.3	1308.9
Rearrangement transition state						
	$\nu_1 (a')$	$\nu_2 (a')$	$\nu_3 (a')$	$\nu_4 (a')$	$\nu_5 (a')$	$\nu_6 (a'')$
SCF						
This work	3155	2806	1637	1408	2645i	637
Ref. 7(b)	3180	2832	1639	1408	2650i	625
DZ + P CI						
Ref. 7(b)	3057	2748	1512	1356	2356i	~ 600 ^d
Molecular products transition state						
	$\nu_1 (a')$	$\nu_2 (a')$	$\nu_3 (a')$	$\nu_4 (a')$	$\nu_5 (a')^c$	$\nu_6 (a'')$
SCF						
This work	3250	2101	1484	819	2295i	1043
Ref. 7(b)	3243	2092	1526	829	2305i	1024
DZ + P CI						
Ref. 7(b)	3263	1939	1555	876	2124i	~ 950 ^d

^aReference 39(a).^bReference 39(b).^cReaction coordinate.^dEstimated.

The MBPT/CCD results suggest that the energy requirements for all three unimolecular processes are approximately equal. Since it is often assumed that even good correlated wave function calculations overestimate barrier heights and underestimate dissociation energies, the MBPT/CCD results imply that the rearrangement to hydroxycarbene is the energetically favored reaction pathway. Such a result agrees with the conclusions of Goddard *et al.*^{5,7(a)} However, basis set changes and the inclusion of triple excitation diagrams may change this result.

It is interesting to note the substantial difference between the energy difference obtained from correlated calculations and the results obtained using just SCF calculations. As stated, the results obtained with MBPT, CCD, and SD-CI imply that the energy requirements for all three reaction pathways are almost equal. The SCF calculations predict that the barriers for dissociation to molecular products (95.7 kcal mol⁻¹) and the barrier for rearrangement to *trans*-hydroxycarbene (99.2 kcal mol⁻¹) differ by a relatively small amount of energy. However, the SCF results imply that each of these barriers is much larger than the barrier for dissociation to radical products (68.6 kcal mol⁻¹). These energy differences demonstrate the importance of including

TABLE X. Predicted energy barriers for formaldehyde reactions.^a

Theoretical method	Reaction		
	1, 2-shift	Molecular products	Radical products
SCF			
This work	95.7	99.2	68.6
Ref. 7(a)	95.2	100.2	... ^b
D-MBPT(4)	86.9	89.0	86.4
SDQ-MBPT(4)	85.7	88.4	85.0
CCD	87.6	90.3	86.1
CI [Ref. 7(a)]			
SD-CI	88.2	92.8	80.0
SD-CI + QC ^c	85.9	88.9	79.1
RMP4			
Ref. 30	86.2	88.0	... ^b

^aUnits: kcal mol⁻¹.^bNo comparable SCF results reported.^cIncludes correction for quadruple excitations based upon Davidson's formula.

correlation energy effects to obtain chemically accurate results.

An additional result of the configuration interaction study was that each decomposition reaction possesses an energy barrier relative to the S_1 band origin. To determine whether the linked-diagram related methods will also predict the existence of this barrier, we must consider the first excited state of formaldehyde.

VI. THE a^3A'' STATE OF FORMALDEHYDE

The ultraviolet absorption spectrum of formaldehyde vapor consists of two band systems: a strong band with apparent origin at 3530 Å (3.454 eV) and a weak band with apparent origin at 3960 Å (3.124 eV). Walsh predicted that these states would have nonplanar structure,⁴³ and this was verified for both the singlet^{44,45} and the triplet^{46,47} states. Jones and Coon derived experimental structures for the excited states, including a specification of the out-of-plane bending angle by a distribution function for each vibrational level of the bending mode.⁴⁸ Recent theoretical studies of the excited states include *ab initio* calculations by Garrison, Schaefer, and Lester,¹⁰ Bell,⁶ and Goddard and Schaefer,⁵ as well as equations-of-motion calculations of the vertical excitation energies.^{17,18} This report complements and extends Bell's work.

Recent calculations^{5,6} used excited state structural parameters determined by optimizing the electronic energy at the SCF level. This study reports structural parameters for the a^3A'' state determined by optimizing the energy at the correlated level. Fourth order, double-excitation MBPT calculations, with core orbitals frozen, were performed for structures obtained by varying the CH and CO bond lengths, the HCH angle, and the out-of-plane bending angle. The CH bond length and the HCH angle were reoptimized after determination of the optimal out-of-plane bending angle. We report the optimal structural parameters in Table XI.

The carbon-hydrogen bond length (1.085 Å) reported here is slightly less than the experimental value (1.0962 Å) while the carbon-oxygen bond length (1.327 Å) exceeds the experimental value (1.307 Å). The optimum HCH and out-of-plane bending angles (118° and 37°12') agree well with the experimental values (118° and 37°54'). Comparison of these theoretical results with Bell's structure⁶ shows that the inclusion of cor-

TABLE XII. Adiabatic excitation energies, $S_0 - T_1$.

	ΔE (eV)	ΔE (kcal mol ⁻¹)
Experiment ^a	3.124	71.9
D-MBPT(4)	3.1455	72.5
SDQ-MBPT(4)	3.1436	72.5
CCD	3.093	71.3
SD-CI ^b	3.01	69.5
SD-CI ^c	2.664	61.4
SCF ^d	2.183	50.3
SCF, this work	1.912	44.1

^aReference 32.

^bReference 5.

^cReference 6.

^dReference 10.

relation effects improves the agreement between theory and experiment.

We report, in Table XII, three theoretical results for the adiabatic excitation energy corresponding to $S_0 - T_1$. Both the D-MBPT(4) and SDQ-MBPT(4) calculations yield 72.5 kcal mol⁻¹ for the excitation energy, while the CCD calculations yielded a value of 71.3 kcal mol⁻¹. These results may be compared to the near Hartree-Fock value, 50.3 kcal mol⁻¹,¹⁰ two SD-CI values 67.4 kcal mol⁻¹⁵ and 68.9 kcal mol⁻¹,⁴⁹ and a value obtained by including the unlinked cluster correction of quadruple-excitation effects 69.5 kcal mol⁻¹.⁵ All the theoretical values compare well with the experimental value 71.9 kcal mol⁻¹.³² None of the theoretical values, however, include any correction for zero-point energy differences that may contribute to the observed value.

Although no effort has been made to determine the structure of formaldehyde in the $A^1A''(S_1)$ state, vertical excitation energies are computed for both the $S_0 - S_1$ and $S_0 - T_1$ transitions. Since the UHF wave function for the S_1 state was contaminated by higher-order spin states, particularly T_1 , the computed excitation energy for this state is expected to be less accurate than that for the T_1 state. Nonetheless, vertical excitation energies for both transitions are presented in Table XIII, along with other theoretical predictions and experimental estimates. The excitation energy for $S_0 - T_1$ is less than that for $S_0 - S_1$, although the latter is probably lower than would be obtained were the ref-

TABLE XI. Formaldehyde structural parameters, a^3A'' state.

	r_{CH} ^a	r_{CO} ^a	HCH	ϕ
Experiment ^b	1.0962	1.3069	118°	37°54'
Theory				
DZP-SCF ^c	1.0779	1.3404	119.67°	38°30'
D-MBPT(4)-FC	1.0848	1.3271	118°	37°12'

^aUnits: angstroms.

^bReference 48.

^cReference 6.

TABLE XIII. Vertical excitation energies for formaldehyde.^a

	$S_0 - T_1$	$S_0 - S_1$
D-MBPT(4)	84.2	89.3
MRD-CI ^b	78.6	87.9
EOM ^c	79.8	93.2
Experiment ^d	83.0	98.2

^aUnits: kcal mol⁻¹.

^bReference 50.

^cReference 18.

^dEstimated excitation energies, Ref. 51.

TABLE XIV. Energy prediction comparisons for photochemical processes.^a

	Reference 5	Reference 7(a)	SDQ-MBPT(4)	CCD	Experiment
$S_0 \rightarrow T_1$	69.5		72.5	71.3	71.9 ^a
D_0	~79.		85.0	86.1	86.0 ± 1 ^b
E_0 (H ₂ CO)	87.5	88.9	88.4	90.3	
E_0	83.9	85.9	85.7	87.6	
$S_0 \rightarrow S_1$	78(est.)		81.0(est.)	79.8(est.)	80.5 ^c

^aReference 32.^bReference 3.^cReference 1.

erence function not spin-contaminated. The difference in the excitation energy predictions is much less than the difference obtained from the equation of motion calculations¹⁷ or estimated from experimental data.⁵¹ However, it should be noted that MRD-CI calculations predict a significantly smaller excitation energy difference (9.3 kcal mol⁻¹)⁵⁰ than is estimated by Chutjian (15.2 kcal mol⁻¹).⁵¹ Since the difference between the two adiabatic excitations is 8.1 kcal mol⁻¹, it seems best to conclude that the $S_0 \rightarrow S_1$ vertical excitation energy remains uncertain.

VII. DISCUSSION

The present calculations demonstrate that linked-diagram related computational methods predict relative energies of small molecular systems to high accuracy. For the results that can be compared with experiment, the dissociation energy for formation of radical products and the $S_0 \rightarrow T_1$ adiabatic excitation energy, the SDQ-MBPT(4) and the CCD results agree well with the experimental values.

It is instructive to review results pertinent to photochemical dissociation and rearrangement of formaldehyde. We collect, in Table XIV, the excitation energy, dissociation energy (D_0), and reaction barrier (E_0) results obtained in this study and in work by Goddard and co-workers.^{5,7(a)} Note that the values for $S_0 \rightarrow S_1$ are estimates based on the theoretical results for the $S_0 \rightarrow T_1$ excitation energy, and the observed $T_1 \rightarrow S_1$ separation. In analyzing the CI results, the authors noted that high level theoretical calculations underestimate dissociation energies and slightly overestimate rearrangement barriers.^{52,53} If it is assumed that the CI calculations underestimate the dissociation energy by 3 to 5 kcal × mol⁻¹, and overestimate the energy barriers by a similar amount, then the CI results imply that the energy requirements for the radical products and molecular products dissociation pathways are similar.⁵ Furthermore, the energy requirements suggest that the hydroxycarbene intermediate cannot be ruled out. The subsequent analytic gradient CI calculations support these results, but each of the energy barriers increases slightly.^{7(a)} Finally, those authors noted that the barriers exceed the estimated adiabatic excitation energy for $S_0 \rightarrow S_1$. Thus, there all small barriers above the S_1 origin to all three photochemical processes.

Examinations of the SDQ-MBPT/CCD results reveals no significant difference from the results of the CI calculations, even though our basis set is somewhat larger than the GS DZ + P basis. However, our SCF result for

the molecular products transition state shows an energy lowering of 3.4 kcal/mol compared to the DZ + P results, suggesting that basis set changes may still be significant in this problem. We cannot make realistic estimates of the errors associated with the barrier calculations, since we have no data for comparison. We assume that these calculations overestimate the energy barriers by 2 to 4 kcal mol⁻¹. With these assumptions, the results of these calculations lead to the same conclusions obtained by GS⁵ and Goddard *et al.*^{7(a)} However, recent work by Frisch *et al.*⁵⁴ suggests that basis set effects and triple excitations lower the computed barriers by ~8 kcal/mol, which is below the origin of the H₂CO excited singlet state.

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